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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : A61F 13/15, 5/44	A1	(11) International Publication Number: WO 91/14413 (43) International Publication Date: 3 October 1991 (03.10.91)
(21) International Application Number: PCT/GB91/00463 (22) International Filing Date: 27 March 1991 (27.03.91) (30) Priority data: 9006953.5 28 March 1990 (28.03.90) GB (71) Applicant (for all designated States except US): DISPOSABLES & DIAPER DEVELOPMENTS LIMITED [GB/GB]; Independence House, Vale Road, Otterspool, Stockport SK6 3LE (GB). (72) Inventor; and (75) Inventor/Applicant (for US only): SHIPLEY, Arthur, Roger [GB/GB]; 8 Oakhill Drive, Prestatyn, Clwyd LL19 9PU (GB). (74) Agent: DUMMETT, Thomas, Ian, Peter; Dummett Copp & Co., 14 The Square, Martlesham Heath, Ipswich, Suffolk IP5 7SL (GB).		(81) Designated States: AT, AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CA, CF (OAPI patent), CG (OAPI patent), CH, CH (European patent), CM (OAPI patent), DE, DE (European patent), DK, DK (European patent), ES, ES (European patent), FI, FR (European patent), GA (OAPI patent), GB, GB (European patent), GR (European patent), HU, IT (European patent), JP, KP, KR, LK, LU, LU (European patent), MC, MG, ML (OAPI patent), MR (OAPI patent), MW, NL, NL (European patent), NO, PL, RO, SD, SE, SE (European patent), SN (OAPI patent), SU, TD (OAPI patent), TG (OAPI patent), US. Published <i>With international search report.</i> <i>Before the expiration of the time limits for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: MATERIALS DISPOSABLE IN WATER (57) Abstract The present invention provides a water disposable material, characterised in that it comprises a substrate which is readily soluble and/or disintegrated in water, which substrate is coated or otherwise protected from water by a surface layer or coating of a material which is readily soluble and/or disintegrable in water when exposed to pH conditions markedly different to those to which it is exposed during normal use. Preferably, the substrate is a water soluble polyvinylalcohol polymer and the coating is an acrylic polymer which is sensitive to alkali. The material can be used in the fabrication of diapers and other fluid absorbent next-the-skin structures which can be disposed of by disintegration in a toilet to which an alkali has been added to raise the pH of the water in the toilet bowl to a value above that encountered during use upon the person.		

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MATERIALS DISPOSABLE IN WATER

The present invention relates to a disposable material, notably to a material which is to be disposed of into the environment, such as a disposable diaper or other body fluid absorbing material or a packaging material.

BACKGROUND TO THE INVENTION:

Many materials are intended for one time use and subsequent disposal. Examples of such materials include diapers, sanitary towels, colostomy bags and other articles intended to absorb body fluids or wastes and where disposal presents a problem from aesthetic and health grounds. It would be desirable if such articles could be disposed of into the sewage system by flushing them down the toilet. However, one of the necessary functions of such articles is that they should contain the fluid and other wastes, and this requires that they be or have a water resistant layer and a measure of wet strength during use. This conflicts with the contradictory requirement that the articles should dissolve and/or break up in water so that they can be flushed down a toilet without blocking the associated pipe work or the drains.

It has been proposed in US Patent No 4 062 451 to form the articles with a water barrier layer formed from a specific silane cross-linked interpolymer which breaks down when the barrier layer is exposed to acid or alkali pH values in the water of a toilet pan outside the range normally encountered during use on the person. It was also proposed in this proposal to impregnate a pad of cellulosic or other fibres with a solution of the resin which then acted as a bonding agent for the fibres. However, this proposal requires the use of a specific polymer material in place of the widely available and cheap materials used hitherto.

Furthermore, in order that the material should be capable of disintegrating sufficiently quickly in the toilet pan to allow it to be flushed away, it was necessary to use extreme pH values, in excess of 12 where an alkali treatment is used to solubilise the film. It was also necessary to use thin films of the polymer, which carries the risk that the article could rupture prematurely. As a result, such a proposal has not been adopted commercially.

It has also been proposed in US Patent No 3 756 232 to use the property of short strand carboxymethylcellulose fibres rapidly to absorb fluids to ensure that an alkali is rapidly taken up in a fibre pad, for example a tampon made from such short strand material, and achieve a high fluids to solids ratio to give rapid reaction of the fibres with the alkali to convert the carboxymethylcellulose or etherified derivative thereof into a water soluble form so that dis-solution or dis-integration of the fibres occurs. However, this proposal makes use of a specific property of a specific physical form of one material. It cannot be applied to other materials in other physical forms. Thus, that proposal cannot be used to treat the polyethylene outer layer of a diaper, which cannot readily be flushed down a toilet without snagging within the pipe work or drains.

It has been proposed in French Patent No 1 572 721 to bond together the fibres of a non-woven material, such as a pad made from cellulosic fibres, using a non-crosslinked resin as the bonding agent. The resin can be applied to the fibres by impregnating the pad with a solution of the resin and drying the impregnated pad. The resin is one which readily solubilises or disintegrates in an acid or alkaline pH environment. However, the material from which the fibres is made is not soluble or decomposed in the acid or alkaline conditions used and the disposability of the

impregnated product relies upon the separation of the fibres to cause disintegration of the pad. Therefore, such a proposal cannot be applied to a woven material or a sheet material. Moreover, it is suggested that the pad
5 incorporate a dry acid or alkali powder within the pad so as to provide the required pH conditions when the pad is immersed in the water of the toilet pan. However, this will also serve to initiate disintegration of the pad during use and the pad must therefore be retained within a
10 non-disintegrable outer member if it is not to disintegrate prematurely. One is then faced with the problem of disposing of the outer member as well the partially disintegrated contents.

There is thus a need for a material which can be used in
15 sheet or woven form to provide a material which can be readily disintegrated in the water of a toilet bowl and yet which has a water containing property so that it can be used to contain bodily or other fluids, optionally in conjunction with a disintegrable absorbent pad.

20 SUMMARY OF THE INVENTION:

Accordingly, the present invention provides a water disposable material which comprises a substrate which is readily soluble and/or disintegrated in water, which substrate is coated or otherwise protected from water by a
25 surface layer or coating of a material which is readily soluble and/or disintegrable in water when exposed to pH conditions markedly different to those to which it is exposed during normal use, notably an alkali sensitive material.

30 Preferably, the material of the invention comprises a substrate in the form of a sheet or fibre or a pad of bonded fibres which are made from a water soluble polymer,

the sheet, pad or fibre having an encasing coating of a polymer which is readily soluble in water having a pH below 6 or above 7.5.

5 The substrate material can also provide the surface layer, for example so that the water disposable material is formed throughout from an alkali soluble or disintegrable material, for example from a acrylic polymer. However, for convenience, the invention will be described hereinafter in terms of a composite material having a surface coating of
10 the pH sensitive material, notably an alkali soluble or disintegrable material, upon a water soluble or disintegrable substrate.

The substrate can be made from a wide range of materials which are water soluble or disintegrable. Thus, the
15 substrate can be a paper or card sheet; a tissue paper; a felted or resin bonded pad or sheet of cellulose or cellulose derivative fibres where the fibres and/or the bonding resin are water soluble: or can be made from a polymer sheet or fibre, for example from polymers or co-
20 polymers of polyvinyl alcohol; poly(alkylene oxide), notably poly- (ethylene oxide); or polyvinylpyrrolidone. Particularly preferred water soluble polymers for present use are polyvinyl alcohols, whose molecular weight can be varied as is known according to the degree of water
25 solubility or disintegration required, and having saponification values in the range 80 to 90%, notably about 88%.

The pH sensitive and soluble or disintegrable polymer for use in the coating is one which has a water resistant or
30 water barrier property under normal pH conditions so that it retains a wet strength or water barrier property, depending upon the end use of the material, but which loses that property upon exposure to pH conditions which are

markedly different from normal. Thus, the coating polymer is preferably one which is substantially insoluble in water under the conditions of normal use, but which is soluble or which disintegrates when exposed to aqueous alkali solutions. Typical alkali sensitive polymers for present use are homo- and co-polymers of acrylic acid and esters thereof, notably C¹-C⁵ alkyl esters of acrylic or methacrylic acids, for example the methyl, ethyl or butyl esters, or acrylonitrile; homo- and co-polymers of carboxy ester lactones, styrene-monoethyl maleate or N,N'-diethylacrylamide; polymers of other types which have been chemically modified by the introduction of solubilising groups such as carboxylic acid, sulphonic acid, sulphite, sulphate, phenolic hydroxy, ester or diamide groups; or polymers which have been rendered soluble by the introduction of interpolymer units into the main polymer chain, for example the silane interpolymers of US Patents Nos 4 062 451 and 3 951 893. Particularly preferred alkali sensitive polymers for present use are the substantially linear co-polymers of from 2 to 6 parts by weight of one or more monomers selected from acrylic acid, ethyl acrylate, butyl acrylate or acrylonitrile with one part by weight of methacrylic acid monomer to give thermoplastic resin products having molecular weights of from 25,000 to 300,000.

The polymers for present use as the surface layer or coating are prepared using conventional techniques, for example by reaction of the appropriate amounts of the relevant acrylic monomers or pre-polymers in the presence of peroxide or sulphonylate polymerisation initiators. Typically, in the case of acrylic materials, the reaction is carried out to yield thermoplastic resins which are substantially free from cross-linking, i.e. are substantially linear polymers, and which have a carboxyl functionality of from 3 to 15 weight percent and an acid

number in the range 30 to 90. If necessary, the resulting resin can be treated in known manner with an alkali or base, for example ammonia, sodium hydroxide, morpholine or an alkylamine (for example triethylamine or triethanol-
5 amine), to impart the desired water solubility under alkaline conditions.

The coating may be a continuous coating which has been achieved by applying a hot melt or a solution in an organic solvent of a suitable acrylic acid homo-polymer or co-
10 polymer to a pre-formed sheet or fibre of the required substrate material, and dried or cured in situ. Alternatively, the polymer of the substrate, eg. the vinyl alcohol polymer, can be co-extruded with the coating resin to form a composite fibre or sheet.

15 In an further alternative, a solution of a suitable monomer or oligomer of the coating polymer can be applied to a preformed sheet or fibre of the substrate material and polymerised to form the coating polymer in situ on the substrate.

20 In an alternative form of the material of the invention, a solution, emulsion or dispersion of the coating polymer is applied by dip coating or spraying to individual fibres of the substrate material to provide a substantially uniform coating upon each fibre. The coated fibres can then be
25 woven into a reticulate sheet material. Alternatively, the coated fibres can be formed into a non-woven material, for example a pad using conventional techniques. Thus, the pad can be formed by air blowing the chopped coated fibres into a randomly orientated pad of the fibres whilst the coating
30 polymer is still drying or curing so as to form a bond between adjacent fibres; by forming the coated fibres into a pad and heating the pad whilst applying pressure to fuse the fibres to one another at the points of contact within

the pad; or by co-extruding the substrate and coating polymers to form a long fibre which is converted into a pad by spinning, flailing or oscillating the fibre as it is extruded to form an intertwined mass of fibre from which
5 the pad may be cut.

The coating polymer can be applied to achieve any desired loading of the polymer on the substrate, according to the nature of the coating polymer and the conditions under which the material of the invention is to be used. Thus,
10 where the material is to be used as a packaging material, it may be desirable to have a comparatively thick coating of polymer on the substrate. Where, the material is to be used in a next-the-person application, for example as a diaper or incontinence pad, it will usually be necessary to
15 have only a thin coating. Thus, the coating polymer can be present in from 5 to 500% by weight of the substrate.

The coating polymer serves to protect the underlying substrate during normal use of the material. Thus, the material of the invention can be used to provide the
20 absorbent pad of a diaper, a potty liner, a nappy liner or other absorbent article for absorbing bodily fluids and/or to provide the water impervious outer layer to such an article which retains the fluid within the pad until it is disposed. The article made from the material of the
25 invention can also take the form of packaging, such as a disposable bag, carton or the like within which material is contained. The substrate can therefore take a wide range of forms, sizes and thicknesses and the coating polymer is preferably of the minimum thickness required to achieve a
30 satisfactory degree of protection commensurate with an adequate speed of dissolution or disintegration when disposal is required.

The coating and substrate polymers can contain other

ingredients which enhance their utility in the end use to which they are to be applied. Thus, the polymers will usually contain stabilizers and plasticizers, anti-oxidants and UV or thermal stabilisers. Where the materials are to
5 be used in packaging of foodstuffs or in next-the-skin applications, it will be appreciated that the appropriate food grade or physiologically acceptable grades of polymer and other ingredients should be used.

The materials of the invention find use in a wide range of
10 applications where disposability of the material is required. Thus, the materials can be used as the water impervious layer of a diaper or sanitary pad or a potty liner; as the absorbent pad in a potty or nappy liner; as the wall material for a colostomy or a blood bag; as a
15 water disposable packaging for a wide range of materials; as containers which are used to release their contents into a fluid after a given delay, for example in the administration of medicaments; or as disposable fabrics, for example for disposable clothing. The materials are
20 preferably used in conjunction with pads of conventional cellulosic or other fibres which are bonded together with a soluble or disintegrable polymer as used as the coating polymer in the materials of the invention. In this way a totally disintegrable diaper can be achieved.

25 We have found that where acrylic polymers are used, they have particularly advantageous alkali solubility properties and that they are particularly suitable for use as the coating polymer since they have good water barrier and wet strength properties at pH values in the range 6 to 8.5, yet
30 readily dissolve and disintegrate when exposed for short periods to pH values above 8.5. Such polymers can therefore be used both as the coating and substrate polymers to enable a wholly soluble pad of fibres and associated water impervious backing sheet to be made from

the one material, with attendant saving in processing costs and complexity.

The invention therefore also provides a structure having fluid absorbent properties characterised in that the structure is made substantially wholly from a homo- or co-polymer of acrylic acid and esters thereof, notably methyl, ethyl or butyl esters of acrylic or methacrylic acids or acrylonitrile; notably the co-polymers of from 2 to 6 parts by weight of one or more monomers selected from acrylic acid, ethyl acrylate, butyl acrylate or acrylonitrile with one part by weight of methacrylic acid monomer to give thermoplastic polymer products having molecular weights of from 25,000 to 300,000 which are substantially free from cross-linking and which have a carboxyl functionality of from 3 to 15 weight percent and an acid number in the range 30 to 90.

Disposal of the material of the invention is achieved by subjecting the material to pH conditions which differ markedly from those to which it is normally exposed. Thus, materials used to absorb or contain bodily fluids or for next to the skin use will normally experience pH values in the range 6 to 8.5, typically 6 to 7.5. In order to dispose of the material by flushing it down a toilet, it will need to be exposed to a more acid or alkaline pH than this, for example in a toilet pan to which an alkali or acid has been added. Typically, the alkaline conditions can be achieved merely by adding the required quantity of a suitable base or alkali to the water. Suitable alkalies or bases include ammonia; sodium or potassium hydroxides or carbonates; or alkyl amines, notably amino alkanols such as 2-amino-2-methyl propanol. Surprisingly, we have found that many household soaps or detergents can often achieve the required alkaline conditions to dissolve or disintegrate the materials of the invention, for example

the alkaline solution of sodium hypochlorite use as a bleaching/sanitising agent in most domestic households.

Where an acid pH is required, this is conveniently achieved by adding mineral acids, for example sulphuric or hydrochloric acids, to the toilet water, or organic acids, for example acetic or citric acids which are readily available to the housewife. Alternatively, many of the toilet sanitising agents used in domestic toilets are formulated to be sufficiently acidic to achieve disintegration of the materials of the invention without the need for added chemicals.

If desired, the required amount of acid or alkali can be incorporated as a dry powder within a portion of the article which would not normally be exposed to moisture so that the required pH conditions can be achieved in the water of the toilet pan without the need for added materials. Thus, the powder can be incorporated in a sachet or the like attached to the material, eg. to the hem of a diaper, which is ruptured by a suitable tear off strip or other means to expose the contents to the water when the material is to be disposed of.

The invention therefore also provides a material or structure of the invention incorporating in a manually releasable form a pH adjusting agent.

Alternatively, a toilet sanitising block or fluid formulation can be prepared so that it is sufficiently acid or alkaline to achieve the desired pH value for the water in the toilet pan.

Thus, from another aspect, the invention provides a toilet sanitising solid or fluid formulation, characterised in that its formulation has been modified so as to provide a

pH value in excess of 7.5, typically from 8.5 to 12, within the water in the toilet pan during use.

- 5 The sanitising agents can be incorporated into a block or other means which is suspended in the toilet cistern or pan so that the sanitising agent is released at each flush of the toilet using conventional techniques. If desired, the sanitising agent can incorporate a colouring or other agent to indicate to a user when the water in the toilet pan is of the desired pH value.
- 10 The invention also provides a method for disposing of a material or structure of the invention, which method comprises placing the material or structure into water; adjusting the pH of the water to a value outside the range at which the material or structure is stable so as to cause
- 15 at least part of the material or structure to dissolve and/or disintegrate; and disposing of the resultant aqueous mixture.

The invention will now be illustrated by way of example only with respect to the following Examples, in which all

20 parts and percentages are given by weight.

Example 1.

A cellulose fibre with strands 6 to 40 mms long is coated with a 20% solution in ethanol of the acrylic acid co-polymer sold under the Trade Mark Carboset 525 by the B F

25 Goodrich Company. The coated strands are formed into an absorbent pad by heating under pressure to bond the fibres together. The Carboset resin is insoluble in water at 25°C, but is readily soluble in 0.5% aqueous ammonium hydroxide solution.

30 The pad is then applied to a sheet formed by co-extruding

the Carboset resin with a polyvinyl alcohol homo-polymer. The polyvinyl alcohol homo-polymer is very readily soluble in water at 25°C. The product is a sheet having a polyvinyl alcohol core within a Carboset resin coating and is
5 resistant to water and bodily fluids.

The composite structure of the pad and sheet can be formed into a diaper which is stable to water and urine, but which readily disintegrates when stirred into water in a toilet pan to which 10 cts of 880 ammonia has been added. The
10 resultant slurry of fibres and urine or faeces can be flushed down the toilet with small risk of blockage of the drains and pipe work.

Example 2:

The process of Example 1 can be repeated except that the
15 fibres are extruded from the Carboset resin and are spun bonded into a pad which is suitable for use with the composite polyvinyl alcohol/Carboset resin sheet or with a sheet wholly extruded from the Carboset resin. In all cases diapers or potty liners made from the Carboset resins
20 readily disintegrate in water treated with the ammonia solution to give a pH of 8 or more and can be flushed away.

Example 3:

A cardboard sheet can be coated with the solution of the Carboset resin of Example 1 to apply a resin coating of 20g
25 dry weight per square metre. The cardboard can be used to form a wide range of cartons using conventional techniques. The cartons will exhibit good wet strength but will readily absorb water after spraying with 5% aqueous sodium hydroxide solution and can be disposed of as a slurry at a
30 land infill site. To aid bacterial decomposition of the cardboard in the ground, a suitable inoculum can be

incorporated into the resin solution applied to the cardboard initially.

Example 4:

5 A toilet sanitising block can be prepared by casting a hot melt composition containing a mazoni soap (70 parts) and 2-amino-2-methyl-1-propanol (30 parts). The block can be suspended under the rim of a toilet pan and the toilet flushed to wash water over the block. The water remaining in the toilet pan when the flush had ceased will have a pH
10 of approximately 9, which is suitable for treatment of a diaper produced in accordance with Example 1.

Example 4:

15 A material which is alkali sensitive is formed by co-extruding a co-polymer of butyl acrylate and methacrylic acid with an outer layer of a mixture of 80 parts of the Carboset resin and 20 parts of the polyethylene resin containing acrylic acid sold under the Trade Mark Dow Primacor. The use of this mixture improves the feel of the resultant sheet or fibre material and results in a material
20 which has a core which is soluble at a pH of 7.5 or more, protected by a material which is less readily soluble so that the material can be used in the manufacture of diapers which can be disintegrated in a toilet as described in Example 1.

CLAIMS:

1. A water disposable material, characterised in that it comprises a substrate which is readily soluble and/or disintegrated in water, which substrate is coated or
5 otherwise protected from water by a surface layer or coating of a material which is readily soluble and/or disintegrable in water when exposed to pH conditions markedly different to those to which it is exposed during normal use.
- 10 2. A material as claimed in claim 1, characterised in that the surface layer or coating is provided by an alkali soluble or disintegrable material.
- 15 3. A material according to claim 1, characterised in that it comprises a substrate in the form of a sheet or fibre or a pad of bonded fibres which are made from a water soluble polymer, the sheet, pad or fibre having an encasing coating of a polymer which is readily soluble in water having a pH below 6 or above 8.5.
- 20 4. A material as claimed in any one of the preceding claims, characterised in that the substrate comprises a polymer or co-polymer of polyvinyl alcohol; a poly(alkylene oxide), notably poly- (ethylene oxide); or a polyvinylpyrrolidone.
- 25 5. A material as claimed in claim 4, characterised in that the substrate comprises a water soluble polyvinyl alcohol having a saponification value in the range 80 to 90%.
- 30 6. A structure having fluid absorbent properties characterised in that the structure is made substantially wholly from an alkali soluble or disintegrable homo- or co-

polymer of acrylic acid and esters thereof in sheet and/or fibre form.

7. A material or structure as claimed in any one of the preceding claims, characterised in that the alkali sensitive material comprises a substantially linear co-polymer of a methyl, ethyl or butyl ester of acrylic with methacrylic acid.
8. A material or structure as claimed in claim 7, characterised in that the co-polymer is a co-polymer of from 2 to 6 parts by weight of one or more monomers selected from acrylic acid, ethyl acrylate, butyl acrylate or acrylonitrile with one part by weight of methacrylic acid monomer.
9. A material or structure as claimed in either of claims 7 or 8, characterised in that said co-polymer is a thermoplastic polymer having a molecular weight of from 25,000 to 300,000 which is substantially free from cross-linking and which has a carboxyl functionality of from 3 to 15 weight percent and an acid number in the range 30 to 90.
10. A material or structure as claimed in any one of the preceding claims, characterised in that the substrate carries from 5 to 500% of the surface layer or coating.
11. A material or structure as claimed in any one of the preceding claims, characterised in that it comprises a fibrous pad in association with a water impervious sheet material at least one of which comprises a water soluble or disintegrable substrate having an alkali sensitive surface layer or coating.
12. A material as claimed in claim 1, characterised in that it comprises a substrate of a water soluble or

disintegrable packaging material having a coating thereon of a pH sensitive material.

13. A material or structure as claimed in any one of the preceding claims, characterised in that the material or
5 structure incorporates a manually releasable pH adjusting agent.
14. A material or structure substantially as hereinbefore described in any one of the examples.
15. A toilet sanitising solid or fluid formulation,
10 characterised in that its formulation has been modified so as to provide a pH value in excess of 7.5, typically from 8.5 to 12, within the water in the toilet pan during use.
16. A method for disposing of a material or structure according to any one of claims 1 to 14, characterised in
15 that the method comprises placing the material or structure into water; adjusting the pH of the water to a value outside the range at which the material or structure is stable so as to cause at least part of the material or structure to dissolve and/or disintegrate; and disposing of
20 the resultant aqueous mixture.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 91/00463

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 A61F13/15 ; A61F5/44		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	A61F	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category [*]	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	FR,A.2 603 189 (SMITHS INDUSTRIES) March 4, 1988	1-4, 10-11, 14-16
Y	see the whole document	5,12 6-9,13
A	---	
X	EP,A,0 142 950 (IMPERIAL CHEMICAL INDUSTRIES) May 29, 1985	1-4, 10-13
A	see page 1, line 19 - line 25 see page 2, line 6 - line 15 see page 3, line 31 - page 4, line 4 see page 6, line 7 - line 13 ---	6,15-16
	--- -/-	
<p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"T" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"I" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
11 JULY 1991	14. 08. 91	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	NICE P. P.R. Nice	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	<p>US,A,3 951 893 (JOHNSON & JOHNSON) April 20, 1976 see column 2, line 43 - line 61 see column 3, line 12 - line 46 see column 7, line 31 - line 40 see column 8, line 61 - line 68 Document cited in the description ---</p>	6-8
Y	<p>World Patents Index, Derwent Publications Ltd., London, GB, 1985, week 8520, classes A97, C03, Q34, accession no. 85-120188 [20], & JP, A, 60061504 (TOKYO ORGANIC CHEMICAL) April 9 1985 ---</p>	5, 12
A	<p>US,A,4 066 583 (D.C. SPAULDING) January 3, 1978 see column 2, line 7 - line 56 see column 3, line 9 - line 11 see column 4, line 30 - line 31 see column 8, line 42 - line 51 ---</p>	6-9

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

GB9100463

SA 46246

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EIPP file on

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR-A-2603189	04-03-88	DE-A- 3727744	17-03-88
		GB-A, B 2195919	20-04-88
		JP-A- 63063456	19-03-88
		US-A- 4868024	19-09-89
EP-A-0142950	29-05-85	AU-B- 576795	08-09-88
		AU-A- 3521984	23-05-85
		JP-A- 60122527	01-07-85
		US-A- 4620999	04-11-86
US-A-3951893	20-04-76	US-A- 4035540	12-07-77
		US-A- 4062451	13-12-77
US-A-4066583	03-01-78	BE-A- 858853	16-01-78
		CA-A- 1100748	12-05-81
		DE-A- 2740169	23-11-78
		FR-A- 2391244	15-12-78
		JP-A- 53141357	09-12-78
		NL-A- 7710383	20-11-78
		SE-A- 7710251	17-11-78